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STONE-GROUND WOOD PULP-REINFORCED POLYPROPYLENE COMPOSITES: WATER UPTAKE AND THERMAL PROPERTIES

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Two of the drawbacks of using natural-based composites in industrial applications are thermal instability and water uptake capacity. In this work, mechanical wood pulp was used to reinforce polypropylene at a level of 20 to 50 wt. %. Composites were mixed by means of a Brabender internal mixer for both non-coupled and coupled formulations. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to determine the thermal properties of the composites. The water uptake behavior was evaluated by immersion of the composites in water until an equilibrium state was reached. Results of water absorption tests revealed that the amount of water absorption was clearly dependent upon the fiber content. The coupled composites showed lower water absorption compared to the uncoupled composites. The incorporation of mechanical wood pulp into the polypropylene matrix produced a clear nucleating effect by increasing the crystallinity degree of the polymer and also increasing the temperature of polymer degradation. The maximum degradation temperature for stone ground wood pulp–reinforced composites was in the range of 330 to 345 ºC.

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INTRODUCTION

The utilization of natural fibers as reinforcement for composite materials based on thermoplastic polymers may be regarded as an emerging sustainable research area in polymer science. In addition to ecological gains such as reducing the environmental impact within the formation, usage and disposal period, further technical and economical advantages may result from this reinforcement strategy. Natural fiber-reinforced polymers provide a reduction of cost and weight of the materials while increasing their recycling capabilities. Nevertheless, when considering specific applications, it is important to understand and take into account that while renewable bio-based materials are more environment-friendly, such materials may lack some performance attributes.

The reinforcement of thermoplastic polymers by means of cellulosic fibers is now a standard technology to improve the mechanical properties such as Young's modulus and tensile strength of polymers, although at the expense of their ductility and impact strength (Ku *et al.* 2011; Kumar *et al.* 2011). Other characteristics such as water absorption and thermal properties must also be studied when considering the possible end-use applications of natural fiber-thermoplastic composites. In this respect, the poor resistance of natural fibers to moisture absorption can cause dimensional instability and undesirable effects on the mechanical properties of composites (Espert *et al.* 2004). The study of this property in detail is fundamental because composites are often placed in

environments where the moisture conditions may change rapidly (Shi and Gardner, 2006). However, the water uptake of natural fiber composites can be reduced considerably by using the appropriate coupling agents to assist with the fiber-matrix adhesion (Zabihzadeh *et al.* 2010). In fact, since mixing the polar and hydrophilic fibers with non-polar and hydrophobic matrix leads to poor dispersion of the fibers due to the strong interfiber hydrogen bonding that holds the fiber together (Bigg *et al.* 1998; John *et al.* 2000), the use of coupling agents has become a standard strategy. This process can either cause hydroxyl groups of fibers to react with coupling agents that have a linear molecular structure similar to the polymer matrix or create a chemical interaction between coupling agents and matrix (Maldas and Kokta 1990). Another problem associated with using cellulosic fibers in composites is the lower processing temperature due to the possibility of degradation of natural fibers, and/or the possibility of volatile emissions that could affect composites properties. In order to avoid this problem, thermal analysis can be used to determine the thermal stability of the materials (Joseph *et al.* 2003). Thermal analysis is an important analytical method in understanding the structure-property relationship of materials and mastering the technology for molecular design and industrial production of different polymeric materials, especially fiber-reinforced composites.

In a previous article (Lopez *et al.* 2012), we reported and discussed the mechanical properties of stone ground wood pulp-reinforced polypropylene composites. In the present work, the water uptake behavior and the thermal properties of those composites were investigated. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to determine the thermal properties, while the water uptake behavior was evaluated by immersion of the composites in water.

EXPERIMENTAL

Materials

The composites were prepared using polypropylene (PP) (Isplen PP090 G2M) provided by Repsol-YPF (Tarragona, Spain) as the polymer matrix. Polypropylene functionalized with maleic anhydride (MAH-PP) (Epolene G3015) with an acid number of 15 mg KOH/g and Mn of 24800 g/mol acquired from Eastman Chemical Products (San Roque, Spain) was used as coupling agent. Stone ground wood pulp (SGWP) derived from softwood (*Pinus radiata*) supplied by Zubialde S.A. (Aizarnazabal, Spain) was used as lignocellulosic reinforcement. With a 27 mm average diameter, a length-weighted fiber length of 0.643 mm and a 40% fines content, SGWP was used as received.

Composites Compounding

PP composite materials comprising 20, 30, 40, and 50 wt. % of stone ground wood fibers, without and with 6 wt. % of MAPP-coupling agent, were prepared. SGWP was dried for 24 h at 105 °C. Then, the components of the composites (SGWP, PP, and MAH-PP) were compounded by means of Brabender plastograph internal mixing. In the formulations containing MAH-PP, this was added into the plastograph together with the polypropylene pellets. The mixing procedure was carried out at 185 ℃ during 10 minutes, and the rotor speed was about 80 rpm for the stone ground wood pulp fibers. The obtained blends were ground by means of a knives mill, dried, and stored at 80 ℃ for

at least 24 h before processing. Test specimens for characterization were obtained by injection-molding by means of a Meteor-40 injection machine.

Water Uptake Behavior

Coupled and uncoupled composites were immersed in distilled water at 23 ºC for different periods of time, and water uptake was determined gravimetrically. The kinetics of water absorption was evaluated applying Eq. 1 or its linearized version, Eq. 2, obtained from Fick theory,

$$\frac{M_t}{M_\infty} = k \cdot t^n \tag{1}$$

$$\log \frac{M_t}{M_\infty} = \log(k) + n \cdot \log(t) \tag{2}$$

where M_t is the water uptake at time t, M_∞ is the water uptake at equilibrium state, and k and n are constants

Differential Scanning Calorimetry

The melting temperature and crystallization behavior of the composites and the neat matrix were investigated using an 820-Mettler Toledo differential scanning calorimeter (DSC) attached with a cooling system under a nitrogen atmosphere. DSC analyses were conducted from 40 to 250 ºC with a heating rate of 10 ºC/min. The specimens were sealed in aluminum pans by pressing, and the prepared samples were placed in the furnace of DSC with an empty reference pan. The heat flow rate as function of temperature was recorded automatically. The melting temperature was identified as the peak point of the DSC curves.

Thermogravimetric Analysis

Thermogravimetric analysis was performed using TGA/851 Mettler Toledo equipment with a heating rate of 10 ºC/min. The samples were heated from 40 to 600 ºC to determine thermal degradation of wood pulp-PP composites and neat PP. All tests were carried out under a nitrogen atmosphere with a flow rate of 60 mL/min.

RESULTS AND DISCUSSION

Water Uptake Behavior

Water uptake was obtained as the increase of the weight of composite samples after immersion in the distilled water at different periods of time. The profiles of water uptake *vs.* immersion time are shown in Fig. 1, and the results of the kinetic study using the Fick's law are summarized in Table 1. The profile and values of the kinetic study of pure polypropylene were not included due to its null capacity for water absorption.
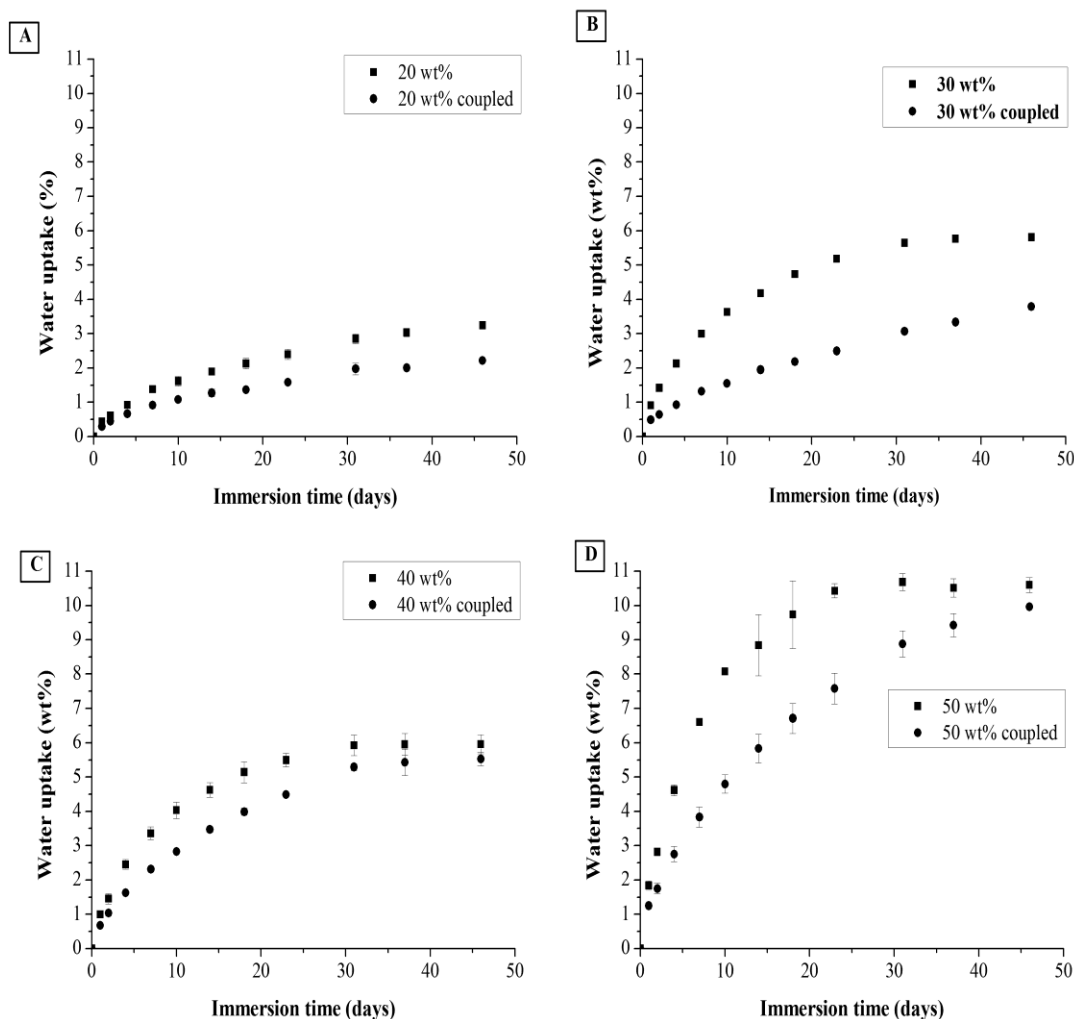
Fig. 1. Water uptake profiles of composites reinforced with stone ground wood pulp, with or without MAPP coupling agent

The incorporation of increasing quantities of fiber content led to increasing capacities for water absorption of the SGWP-composites. This result is attributed to the formation of an incompatible blend from the two components and the incorporation of a hydrophilic reinforcement inside a hydrophobic polymer matrix. Polypropylene is a polymer material based on aliphatic CH-CH_2-(CH_3)- structures; such a structure lacks any capacity to interact with polar species such as water or hydroxyl-functionalized reinforcements as cellulosic fibers. The very different chemical structure of cellulosic fibers means that the material has a low compatibility with aliphatic matrices, as has been well explained in the literature (Mutjé *et al.* 2006; Méndez *et al.* 2007). The incompatibility involves the establishment of non-chemical anchored interphases representing a physical path for water diffusion.

On the other hand, the incorporation of a hydrophilic reinforcement induces capacity to interact with water. Each structural unit of cellulose, known as D-glucopyranose, has three hydroxyl groups to interact with polar bonds. Both effects, chemical incompatibility and polarity of stone groundwood pulp, are responsible for the

increase of M_∞ from 3.2 to 10.68 wt.% when the material is reinforced with 20 and 50 wt. % of stone ground wood pulp, respectively.

Table 1. Parameters of Fick's Law and Moisture Diffusion Coefficient of Composites Reinforced with Stone Groundwood Pulp

Formulations	K (x 10^{-4} s$^{-1/2}$)	n	M_∞ (wt. %)	D (x 10^{-14} m$^2 \cdot$s^{-1})
20	3.6	0.519	3.24	26.6
20 coupled	2.7	0.537	2.21	14.9
30	3.7	0.519	5.81	27.7
30 coupled	2.4	0.546	3.78	12.1
40	4.2	0.559	5.96	35.0
40 coupled	3.7	0.571	5.52	7.9
50	4.4	0.535	10.68	39.1
50 coupled	1.7	0.566	9.95	6.2

The low chemical compatibility between the aliphatic polymer matrix and the reinforcement is responsible for different limitation of the composite material, such as decreasing mechanical strength. This limitation can be minimized by the incorporation of coupling agents such as maleated-grafted polypropylene (MAPP). This component establishes chemical bonding between both components of the composite, which improves the mechanical properties of the composites significantly (Méndez *et al.* 2007). But, the incorporation of MAPP also can reduce the water absorption capacity of composites reinforced with cellulosic fibers, as shown in Fig. 1. The addition of 6 wt. % of MAPP (with respect to the fiber content) decreased the interaction with water in all the cases. This result can be justified by the reduction of phase separation between the polymer and the reinforcement due to the formation of chemical linkages between MAPP and cellulose. The decrease of the gaps between both components reduces the path for water absorption, decreasing the capacity of water access to the inner part of the sample. In the same sense, the establishment of ester bonding between MAPP and cellulose decreases the population of –OH groups, thus decreasing the water uptake capacity.

All of these results are justified mathematically by the Fick's law through the determination of the moisture diffusion coefficient (D).

$$\left(\frac{M_t}{M_0}\right) = \frac{4}{L} \cdot \left(\frac{D}{\pi}\right)^{0.5} \cdot t^{0.5} \tag{3}$$

In Eq. 3, L is the thickness of the sample, and t is the exposition time. The diffusion coefficient (D) represents the ability of solvent molecules, in our case water, to penetrate inside the composite structure (Espert *et al.* 2004).

As it can be observed from the experimental values listed in Table 1, all the materials tested showed a Fickian behavior with values of n close to 0.5 (see Eqs. 1 and 2). This result is consistent with a Case I, or Fickian diffusion, in which the rate of diffusion is much less than that of the polymer segment mobility. The equilibrium inside the polymer is rapidly reached, and it is maintained with independence from time.

The incorporation of higher content of fibers led to higher values of the diffusion coefficients (D) for all the different composites. This result is in agreement with results

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reported for other lignocellulosic fiber-reinforced composites (Najafi and Khademi-Eslam 2011; Kord 2011). The explanation to this behavior can be found in the hydrophilic character of natural fibers. As a result of this hydrophilicity, the inclusion of water molecules inside the composite material is favored, as demonstrated by the kinetics of the diffusion processes summarized in Table 1. From the point of view of the incorporation of MAPP as coupling agent, the moisture diffusion coefficient decreased with the increase of MAPP content. When the reinforcing percentage was low, *i.e.* 20 wt. %, this result was opposite and attributed to the low quantity of MAPP added to the system, since its net addition depended on fiber content. This result is consistent with the formation of thinner interphases between the polymer and the reinforcement, which reduces the diffusion of water through the material.

Thermal Properties

The DSC thermograms of neat PP and PP-composites reinforced with 20 and 40 wt. % of SGW (with and without MAPP coupling agent) are presented in Fig. 2. In addition, the main parameters determined through DSC analysis (melting temperature, melting enthalpy, and degree of crystallinity) of each of the materials evaluated are summarized in Table 2.

The degree of crystallinity (X_c) of a semicrystalline polymer can be determined according to Eq. 4, where ΔH_m is the melting enthalpy of a polymer (calculated from the integral of the endothermal peak in the DSC curve), and ΔH^0_m is the heat of fusion of 100% crystalline polypropylene. A literature value of 204 J/g for ΔH^0_m was used (Areizaga *et al.* 2002).

$$X_c = \frac{\Delta H_m}{\Delta H_m^{100\%}} \tag{4}$$

However, since the degree of crystallinity of a material is only applied to the polymeric fraction of a composite, a correction factor was applied to the value of X_c in order to take into consideration the amount of polymer in the composite. Thus, values of X_c reported were obtained from Eq. 5, where (w^F) corresponds to the weight percentage of fiber in the composite.

$$X_c = \frac{\Delta H_m}{\Delta H_m^{100\%}} \times \frac{100}{(100 - w^F)} \tag{5}$$

Results of DSC experiments gave evidence that the incorporation of SGWP caused a decrease in the melting temperature of the composites. Conversely, the crystalline degree was raised by fiber incorporation when incorporated to the PP matrix. It is accepted that cellulosic fibers can act as a nucleating agent for crystallization of PP matrix. In turn, this nucleation capacity increases the crystallization rate and may lead to higher crystallization degrees through trans-crystallization on high fiber surface available (Amash and Zugenmaier 2000; Joseph *et al.* 2003).
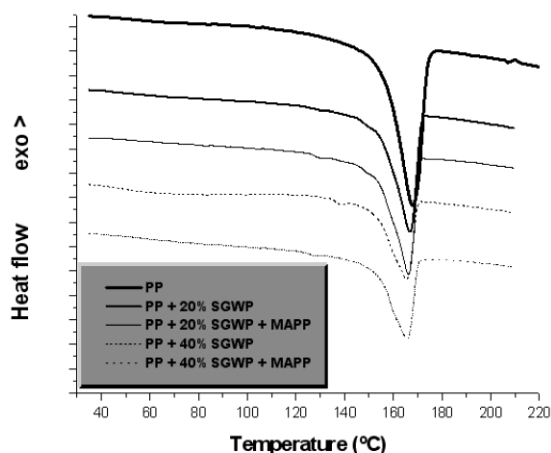
Fig. 2. Differential scanning calorimetry of PP and SWGP – reinforced composites

Table 2. Melting Temperature, Melting Enthalpy, and Crystalline Degree of PP and SGWP-Reinforced Composites With and Without MAPP Coupling Agent

Material			Melting Temperature	Melting Enthalpy	Degree of Crystallinity
Matrix	% SGWP	MAPP	(ºC)	(J·g-1)	(%)
PP	-	No	198,0	99,7	48,9
PP	20%	No	159,3	102,8	63,0
PP	20%	Yes	160, 8	111,0	68,0
PP	40%	No	157,1	80,1	65,4
PP	40%	Yes	158,3	77,1	63,0

The effect caused by the addition of the MAPP coupling agent on the thermal properties of composites was not as straightforward. Thus, the crystalline degree of composites reinforced with 20% SGWP increased when coupling agent was added to the formulation. However, this increase was not detected on composites with 40% SGWP. The nucleation effect of reinforcement is well documented, whilst the effect of coupling agents also tends to provide analogous results (Joseph *et al.* 2003; Girones *et al.* 2007).

Figure 3 presents the results for TGA analysis of neat PP, showing that the thermal degradation of polypropylene took place in a single process starting at 350 ºC with a maximum degradation rate at 435 ºC. At 460 ºC, PP was completely decomposed, presenting ash content below 2%. The TGA thermograms of SGWP–reinforced composites are also represented in Fig. 3. Unlike the results for pure PP, the weight loss in composite materials took place in two steps. The first one, corresponding to the degradation of SGWP, took place between 260 and 350 ºC, with maximum degradation rates in the range of 330 to 350 ºC. Due to the decomposition of the glycosidic bonds and the depolymerisation of hemicelluloses, decomposition of cellulose and hemicellulose typically occurred at 300 to 350 ºC. Thus, the fact of degradation of SGWP starting at lower temperatures gives evidence of the presence of lignin. The second weight loss process corresponds to the decomposition of PP. It is also noteworthy that this stage took place at slightly higher temperatures for SGWP-reinforced composites than for neat PP.
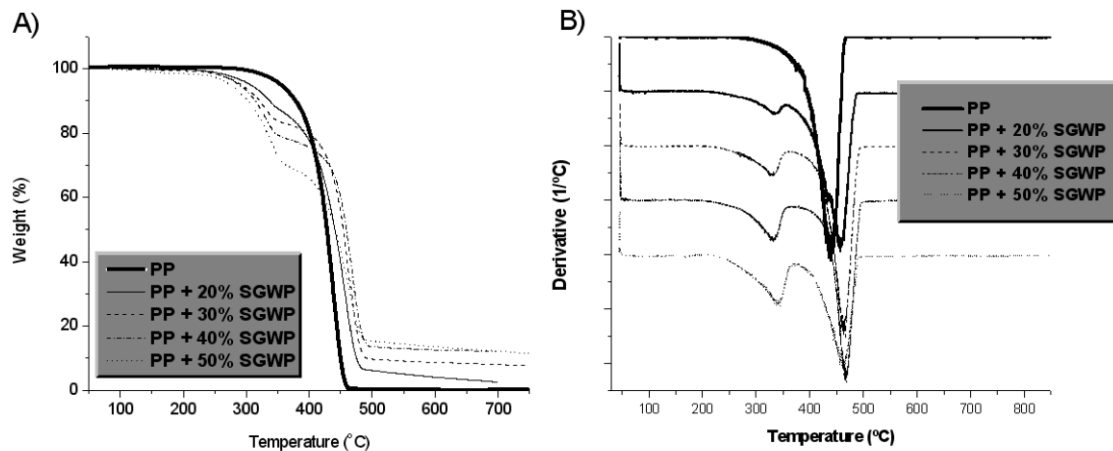
Fig. 3. TGA (a) and DTGA (b) of PP and SWGP-reinforced composites containing 20 to 50% w/w of reinforcement

The effect of the coupling agent on the degradation temperature of composites is presented in Fig. 4. If comparisons are made between coupled and uncoupled composites, one could detect a slight effect caused by MAPP on the thermal stability of the composites. Thus, even though the effect was minimal, results of the TGA experiments suggest that coupling agent might enhance the thermal stability of the material. However, the reason for such effect remains unclear.
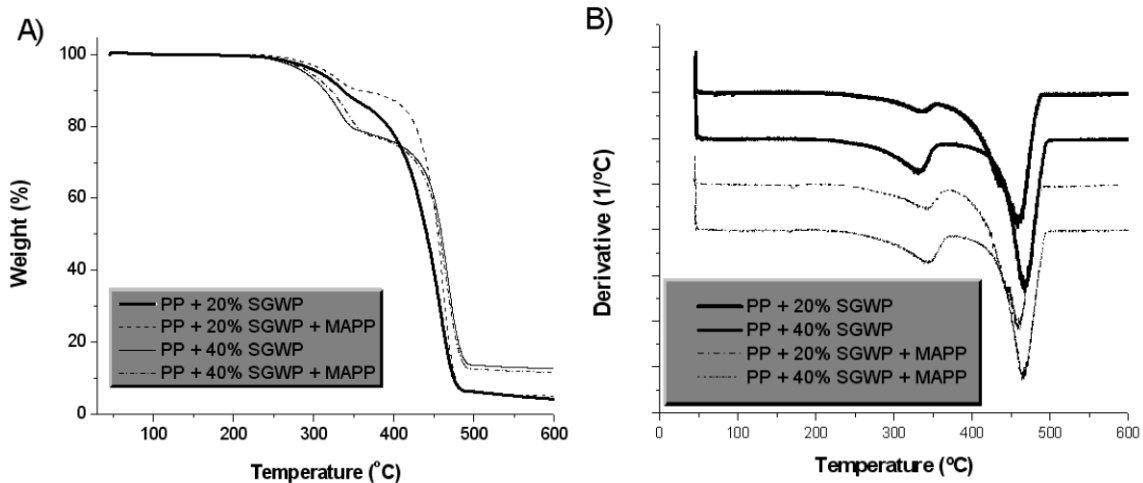

Fig. 4. Effect of MAPP coupling agent on thermal stability of SGWP-reinforced PP composites: TGA (a) and DTGA (b)

CONCLUSIONS

1. Results of water absorption tests revealed that the amount of water absorbed was clearly dependent upon the fiber content, and the coupled composites showed lower water absorption compared to the uncoupled composites. This indicates that MAPP coupling agent plays an important role inhibiting the sorption of the water molecules.

2. The water uptake kinetics of stone ground wood pulp composites followed Fick's law, with a maximum absorption level that increased with the wood content up to 10.68% for composites comprising 50 wt. % of wood fiber. The use of compatibilizing agent reduced the diffusion coefficient of water into the composite, especially at higher MAPP content.

3. The plain polypropylene matrix showed a degradation temperature of about 435 ºC, which was increased to 465 ºC with the wood pulp reinforcement; meanwhile stone ground wood pulp started degrading at 260 ºC, with a maximum degradation ratio between 330 to 345 ºC.

4. The incorporation of stone groundwood pulp into the polypropylene matrix produced an increase on the crystalline degree of the polymer, as well as a decrease on its melting temperature. Increase in the polymer crystallinity helped to increase the mechanical performance of the final composite.

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